

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 251 673
A1

F1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 87305611.3

(51) Int. Cl. 4: D21F 11/00

(22) Date of filing: 24.06.87

(30) Priority: 27.06.86 US 879673

(43) Date of publication of application:
07.01.88 Bulletin 88/01(64) Designated Contracting States:
BE DE FR GB IT NL SE

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(54) Process for making wet-laid structures containing individualized, stiffened fibers.

(57) A process for making wet-laid structures containing individualized, stiffened fibers. The wet-laid structures are obtained by: providing a slurry containing individualized, crosslinked fibers; depositing the slurry of fibers on a foraminous forming wire; directing at least one stream of fluid upon the fibers such that the fluid disperses flocculations of fibers and also inhibits the formation of additional flocculations of the fibers; and setting the fibers into a sheeted form while the fibers are in a substantially unflocculated condition. The step of setting the fibers into sheeted form may be performed by pressing the fibers against the forming wire with a screened roll, such as a cylindrical Dandy Roll. Preferably, a plurality of streams of fluid having sequentially decreasing volumetric flow rates are directed upon the fibers. The individualized, stiffened fibers may also be mixed with conventional, stiffened fibers or highly refined, stiffened fibers while in slurry form.

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PROCESS FOR MAKING WET-LAID STRUCTURES CONTAINING INDIVIDUALIZED, STIFFENED FIBERS

FIELD OF INVENTION

This invention is concerned with individualized, stiffened fibres and processes for forming such fibers into wet-laid structures.

BACKGROUND OF THE INVENTION

Fibers stiffened in substantially individualized form and various methods for making such fibers have been described in the art. The term "individualized, stiffened, crosslinked fibers", refers to cellulosic fibers that have primarily intrafiber chemical crosslink bonds. That is, the crosslink bonds are primarily between cellulose molecules of a single fiber, rather than between cellulose molecules of separate fibers. Individualized, crosslinked fibers and other individualized, stiffened fibers are generally regarded as being useful in absorbent product applications. In general, three categories of processes have been reported for making individualized, stiffened fibers by forming intrafiber crosslink bonds. These processes, described below, are herein referred to as 1) dry crosslinking processes; 2) aqueous solution crosslinking processes, and 3) substantially non-aqueous solution crosslinking processes. The fibers themselves and absorbent structures containing individualized, stiffened fibers generally exhibit an improvement in at least one significant absorbency property relative to conventional, uncrosslinked fibers. Often, this improvement in absorbency is reported in terms of absorbent capacity. Additionally, absorbent structures made from individualized crosslinked fibers generally exhibit increased wet resilience and increased dry resilience relative to absorbent structures made from uncrosslinked fibers. The term "resilience" shall hereinafter refer to the ability of pads made from cellulosic fibers to return toward an expanded original state upon release of a compressional force. Dry resilience specifically refers to the ability of an absorbent structure to expand upon release of compressional force applied while the fibers are in a substantially dry condition. Wet resilience specifically refers to the ability of an absorbent structure to expand upon release of compressional force applied while the fibers are in a moistened condition. For the purposes of this invention and consistency of disclosure, wet resilience shall be observed and reported for an absorbent structure moistened to saturation.

Processes for making individualized, crosslinked fibers with dry crosslinking technology are described in U.S. Patent No. 3,224,926 issued to L. J. Bernardin on December 21, 1965. Individualized, crosslinked fibers are produced by impregnating swollen fibers in an aqueous solution with crosslinking agent, dewatering and defiberizing the fibers by mechanical action, and drying the fibers at elevated temperature to effect crosslinking while the fibers are in a substantially individual state. The fibers are inherently crosslinked in an unswollen, collapsed state as a result of being dehydrated prior to crosslinking. Processes as exemplified in U.S. Patent Nos. 3,224,926, wherein crosslinking is caused to occur while the fibers are in an unswollen, collapsed state, are referred to as processes for making "dry crosslinked" fibers. Dry crosslinked fibers are characterized by low fluid retention values (FRV). It is suggested in U.S. Patent No. 3,440,135, Issued to R. Chung on April 22, 1969, to soak the fibers in an aqueous solution of a crosslinking agent to reduce interfiber bonding capacity prior to carrying out a dry crosslinking operation similar to that described in U.S. Patent No. 3,224,926. This time consuming pretreatment, preferably between about 16 and 48 hours, is alleged to improve product quality by reducing nit content resulting from incomplete defibration.

Processes for producing aqueous solution crosslinked fibers are disclosed, for example, in U.S. Patent No. 3,241,553, Issued to F. H. Steiger on March 22, 1966. Individualized, crosslinked fibers are produced by crosslinking the fibers in an aqueous solution containing a crosslinking agent and a catalyst. Fibers produced in this manner are hereinafter referred to as "aqueous solution crosslinked" fibers. Due to the swelling effect of water on cellulosic fibres, aqueous solution crosslinked fibers are crosslinked while in an uncollapsed, swollen state. Relative to dry crosslinked fibers, aqueous solution crosslinked fibers as disclosed in U.S. Patent No. 3,241,553 have greater flexibility and less stiffness, and are characterized by higher fluid retention value (FRV). Absorbent structures made from aqueous solution crosslinked fibers exhibit lower wet and dry resilience than pads made from dry crosslinked fibers.

In U.S. Patent No. 4,035,147, issued to S. Sangeris, G. Guiray and J. Quere on July 12, 1977, a method is disclosed for producing individualized, crosslinked fibers by contacting dehydrated, nonswollen fibers with crosslinking agent and catalyst in a substantially nonaqueous solution which contains an insufficient amount of water to cause the fibers to swell. Crosslinking occurs while

the fibers are in this substantially nonaqueous solution. This type of process hereinafter be referred to as a nonaqueous solution crosslinked process; and the fibers thereby produced, shall be referred to as nonaqueous solution crosslinked fibers. Like dry crosslinked fibers, nonaqueous solution crosslinked fibers are highly stiffened by crosslink bonds, and absorbent structures made therefrom exhibit relatively high wet and dry resilience.

Crosslinked fibers as described above are believed to be useful for lower density absorbent product applications such as diapers and also higher density absorbent product applications such as catamenials. However, such fibers have not provided sufficient absorbency benefits, in view of their detriments and costs, over conventional fibers to result in significant commercial success.

One difficulty which has been experienced with respect to individualized, crosslinked fibers, especially dry crosslinked and nonaqueous solution crosslinked fibers, is that the fibers rapidly flocculate upon wet-laying on a foraminous forming wire. This has hindered formation of absorbent wet laid structures as well as formation of densified sheets which would facilitate economic transport of the fibers to a converting plant.

It is an object of this invention to provide improved processes for forming individualized, crosslinked fibers into wet-laid structures.

SUMMARY OF THE INVENTION

It has been found that the wet-laid structures containing individualized, stiffened fibers may be made according to a process which includes the steps of:

- a) providing a slurry containing individualized, stiffened fibers;
 - b) depositing the slurry of fibers on a foraminous forming wire;
 - c) directing at least one stream of fluid upon the fibers such that the fluid disperses flocculations of fibers and also inhibits the formation of additional flocculations of the fibers; and
 - d) setting the fibers into a sheeted form while the fibers are in a substantially unflocculated condition.
- The step of setting the fibers into sheeted form may be performed by pressing the fibers against the forming wire with a screened roll, such as a cylindrical Dandy Roll. Preferably, a plurality of streams of fluid having sequentially decreasing volumetric flow rates are directed upon the fibers. The individualized, stiffened fibers may also be mixed with conventional, unstiffened fibers or highly refined, unstiffened fibers while in slurry form.

DETAILED DESCRIPTION OF THE INVENTION

Individualized, stiffened fibers made from cellulosic fibers of diverse natural origin are applicable to the invention. Digested fibers from softwood, hardwood or cotton linters are preferably utilized. Fibers from Esparto grass, bagasse, kemp, flax, and other lignaceous and cellulosic fiber sources may also be utilized as raw material in the invention. The fibers may be supplied in slurry, unsheeted or sheeted form. Fibers supplied as wet lap, dry lap or other sheeted form are preferably rendered into unsheeted form by mechanically disintegrating the sheet, preferably prior to contacting the fibers with the crosslinking agent. Also, preferably the fibers are provided in a wet or moistened condition. Most preferably, the fibers are never-dried fibers. In the case of dry lap, it is advantageous to moisten the fibers prior to mechanical disintegration in order to minimize damage to the fibers. Also applicable to the present invention are individual fibers of synthetic origin which tend to flocculate in solution due to fiber chemistry, geometry or a combination of these or other factors.

The optimum cellulose fiber source utilized in conjunction with this invention will depend upon the particular end use contemplated. Generally, pulp fibers made by chemical pulping processes are preferred. Completely bleached, partially bleached and unbleached fibers are applicable. It may frequently be desired to utilize bleached pulp for its superior brightness and consumer appeal. In one novel embodiment of the invention, hereinafter more fully described, the fibers are partially bleached, crosslinked, and then bleached to completion. For products such as paper towels and absorbent pads for diapers, sanitary napkins, catamenials, and other similar absorbent paper products, it is especially preferred to utilize fibers from southern softwood pulp due to its premium absorbency characteristics. Any individualized, stiffened fibers which flocculate in solution are intended to be within the scope of this invention. These include the fibers made according to the dry crosslinking processes and nonaqueous solution crosslinking processes disclosed in the Background of The Invention. Also contemplated are individualized, stiffened fibers treated with resins or other polymeric compounds as exemplified in U.S. Patent No. 3,819,470, issued to Shaw, D. L., et al, on June 25, 1974 and U.S. Patent No. 3,756,913, issued to Wodka, E. A., September 4, 1973. This invention is believed to be most useful for individualized stiffened fibers which have twisted, curled configurations. Processes for making such fibers with monomeric crosslinking agents are discussed below.

Crosslinking agents available to the present development which are preferred included C_2 - C_8 dialdehydes, as well as acid analogues of such dialdehydes wherein the acid analogue has at least one aldehyde group, and oligomers of such dialdehydes and acid analogues. These compounds are capable of reacting with at least two hydroxyl groups in a single cellulose chain or on proximately located cellulose chains in a single fiber. Those knowledgeable in the area of crosslinking agents will recognize that the dialdehyde crosslinking agents described above will be present, or may react in a variety of forms, including the acid analogue and oligomer forms identified above. All such forms are meant to be included within the scope of the preferred embodiments. Reference to a particular crosslinking agent shall therefore hereinafter refer to that particular crosslinking agent as well as other forms as may be present in an aqueous solution. Particular crosslinking agents contemplated for use with the invention are glutaraldehyde, glyoxal, and glyoxylic acid. Glutaraldehyde is especially preferred, since it has provided fibers with the highest levels of absorbency and resiliency, is believed to be safe and non-irritating to human skin when in a reacted, crosslinked condition, and has provided the most stable, crosslink bonds.

It has been unexpectedly discovered that superior absorbent pad performance may be obtained at crosslinking levels which are substantially lower than crosslinking levels previously practiced. In general, unexpectedly good results are obtained for absorbent pads made from individualized, crosslinked fibers having between 0.5 mole % and about 3.5 mole % crosslinking agent, calculated on a cellulose anhydroglucose molar basis, reacted with the fibers.

Preferably, the crosslinking agent is contacted with the fibers in a liquid medium, under such conditions that the crosslinking agent penetrates into the interior of the individual fiber structures. However, other methods of crosslinking agent treatment, including spraying of the fibers while in individualized, fluffed form, are also within the scope of the invention.

Generally, the fibers will also be contacted with an appropriate catalyst prior to crosslinking. The type, amount, and method of contact of catalyst to the fibers will be dependent upon the particular crosslinking process practiced. These variable will be discussed in more detail below.

Once the fibers are treated with crosslinking agent and catalyst, the crosslinking agent is caused to react with the fibres in the substantial absence of interfiber bonds, i.e., while interfiber contact is maintained at a low degree of occurrence relative to unfluffed pulp fibers, or the fibers are submerged in a solution that does not facilitate the

formation of interfiber bonding, especially hydrogen bonding. This results in the formation of crosslink bonds which are intrafiber in nature. Under these conditions, the crosslinking agent reacts to form crosslink bonds between hydroxyl groups of a single cellulose chain or between hydroxyl groups of proximately located cellulose chains of a single cellulosic fiber.

Although not presented or intended to limit the scope of the invention, it is believed that the crosslinking agent reacts with the hydroxyl groups of the cellulose to form hemiacetal and acetal bonds. The formation of acetal bonds, believed to be the desirable bond types providing stable crosslink bonds is favored under acidic reaction conditions. Therefore, acid catalyzed crosslinking conditions are highly preferred for the purposes of this invention.

The fibers are preferably mechanically defibrated into a low density, individualized, fibrous form known as "fluff" prior to reaction of the crosslinking agent with the fibers. Mechanical defibration may be performed by a variety of methods which are presently known in the art or which may hereinafter become known. Mechanical defibration is preferably performed by a method wherein knot formation and fiber damage are minimized. One type of device which has been found to be particularly useful for defibrating the cellulosic fibers is the three stage fluffing device described in U.S. Patent No. 3,987,968, issued to D. R. Moore and O. A. Shields on October 26, 1976.

The fluffing device described in U.S. Patent No. 3,987,968 subjects moist cellulosic pulp fibers to a combination of mechanical impact, mechanical agitation, air agitation and a limited amount of air drying to create a substantially knot-free fluff. The individualized fibers have imparted thereto an enhanced degree of curl and twist relative to the amount of curl and twist naturally present in such fibers. It is believed that this additional curl and twist enhances the resilient character of absorbent structures made from the finished, crosslinked fibers. It is also believed that this additional curl and twist enhances the degree of flocculation of the individualized, crosslinked fibers.

Other applicable methods for defibrating the cellulosic fibers include, but are not limited to, treatment with a Waring blender and tangentially contacting the fibers with a rotating disk refiner or wire brush. Preferably, an air stream is directed toward the fibers during such defibration to aid in separating the fibers into substantially individual form.

Regardless of the particular mechanical device used to form the fluff, the fibers are preferably mechanically treated while initially containing at least 20% moisture, and preferably containing between about 40% and 60% moisture.

Mechanical refining of fibers at high consistency or of partially dried fibers may also be utilized to provide curl and twist to the fibers in addition to curl or twist imparted as a result of mechanical defibration.

The fibers made according to the present invention have unique combinations of stiffness and resiliency, which allow absorbent structures made from the fibers to maintain high levels of absorptivity, and exhibit high levels of resiliency and an expansionary responsiveness to wetting of a dry, compressed absorbent structure. In addition to having the levels of crosslinking within the stated ranges, the crosslinked fibers are characterized by having water retention values (WRV's) of less than 60, and preferably between 28 and 45, for conventional, chemically pulped, papermaking fibers. The WRV of a particular fiber is indicative of the level of crosslinking and the degree of swelling of the fiber at the time of crosslinking. Those skilled in the art will recognize that the more swollen a fiber is at the time of crosslinking, the higher the WRV will be for a given level of crosslinking. Very highly crosslinked fibers, such as those produced by the prior known dry crosslinking processes previously discussed, have been found to have WRV's of less than 25, and generally less than about 20. The particular crosslinking process utilized will, of course, affect the WRV of the crosslinked fiber. However, any process which will result in crosslinking levels and WRV's within the stated limits is believed to be, and is intended to be, within the scope of this invention. Applicable methods of crosslinking include dry crosslinking processes and nonaqueous solution crosslinking processes as generally discussed in the Background Of The Invention. Certain preferred dry crosslinking and nonaqueous solution crosslinking processes, within the scope of the present invention, will be discussed in more detail below. Aqueous solution crosslinking processes wherein the solution causes the fibers to become highly swollen will result in fibers having WRV's which are in excess of 60. These fibers will provide insufficient stiffness and resiliency for the purposes of the present invention.

Specifically referring to dry crosslinking processes, individualized, crosslinked fibers may be produced from such a process by providing a quantity of cellulosic fibers, contacting a slurry of the fibers with a type and amount of crosslinking agent as described above, mechanically separating, e.g., defibrating, the fibers into substantially individual form, and drying the fibers and causing

the crosslinking agent to react with the fibers in the presence of a catalyst to form crosslink bonds while the fibers are maintained in substantially individual form. The defibration step, apart from the drying step, is believed to impart additional curl. Subsequent drying is accompanied by twisting of the fibers, with the degree of twist being enhanced by the curled geometry of the fiber. As used herein, fiber "curl" refers to the geometric curvature of the fiber about the longitudinal axis of the fiber. "Twist" refers to a rotation of the fiber about the perpendicular cross-section of the longitudinal axis of the fiber. For exemplary purposes, and without intending to specifically limit the scope of the invention, individualized, crosslinked fibers within the scope of the invention having an average of about 6 (six) twists per millimeter of fiber have been observed.

Maintaining the fibers in substantially individual form during drying and crosslinking allows the fibers to twist during drying and thereby be crosslinked in such twisted, curled state. Drying fibers under such conditions that the fibers may twist and curl is referred to as drying the fibers under substantially unrestrained conditions. On the other hand, drying fibers in sheeted form results in dried fibers which are not twisted and curled as fibers dried in substantially individualized form. It is believed that interfiber hydrogen bonding "restrains" the relative occurrence of twisting and curling of the fiber.

There are various methods by which the fibers may be contacted with the crosslinking agent and catalyst. In one embodiment, the fibers are contacted with a solution which initially contains both the crosslinking agent and the catalyst. In another embodiment, the fibers are contacted with an aqueous solution of crosslinking agent and allowed to soak prior to addition of the catalyst. The catalyst is subsequently added. In a third embodiment, the crosslinking agent and catalyst are added to an aqueous slurry of the cellulosic fibers. Other methods in addition to those described herein will be apparent to those skilled in the art, and are intended to be included within the scope of this invention. Regardless of the particular method by which the fibers are contacted with crosslinking agent and catalyst, the cellulosic fibers, crosslinking agent and catalyst are preferably mixed and/or allowed to soak sufficiently with the fibers to assure thorough contact with and impregnation of the individual fibers.

In general, any substance which catalyzes the crosslinking mechanism may be utilized. Applicable catalysts include organic acids and acid salts. Especially preferred catalysts are salts such as aluminum, magnesium, zinc and calcium salts of chlorides, nitrates or sulfates. One specific example

of a preferred salt is zinc hexahydrate. Other catalysts include acids such as sulfuric acid, hydrochloric acid and other mineral and organic acids. The selected catalyst may be utilized as the sole catalyzing agent, or in combination with one or more other catalysts. It is believed that combinations of acid salts and organic acids as catalyzing agents provide superior crosslinking reaction efficiency. Unexpectedly high levels of reaction completion have been observed for catalyst combinations of zinc nitrate salts and organic acids, such as citric acid, and the use of such combinations is preferred. Mineral acids are useful for adjusting pH of the fibers while being contacted with the crosslinking agent in solution, but are preferably not utilized as the primary catalyst.

The optimum amount of crosslinking agent and catalyst utilized will depend upon the particular crosslinking agent utilized, the reaction conditions and the particular product application contemplated.

The amount of catalyst preferably utilized is, of course, dependent upon the particular type and amount of crosslinking agent and the reaction conditions, especially temperature and pH. In general, based upon technical and economic considerations, catalyst levels of between 10 wt. % and 60 wt. %, based on the weight of crosslinking agent added to the cellulosic fibers, are preferred. For exemplary purposes, in the case wherein the catalyst utilized is zinc nitrate hexahydrate and the crosslinking agent is glutaraldehyde, a catalyst level of 30 wt. %, based upon the amount of glutaraldehyde added, is preferred. Most preferably, between 5% and 30%, based upon the weight of the glutaraldehyde, of an organic acid, such as citric acid, is also added as a catalyst. It is additionally desirable to adjust the aqueous portion of the cellulosic fiber slurry or crosslinking agent solution to a target pH of between pH 2 and about pH 5, more preferably between pH 2.5 and pH 3.5, during the period of contact between the crosslinking agent and the fibers.

The cellulosic fibers should generally be dewatered and optionally dried. The workable and optimal consistencies will vary depending upon the type of fluffing equipment utilized. In the preferred embodiments, the cellulosic fibers are dewatered and optimally dried to a consistency of between 30% and 80%. More preferably, the fibers are dewatered and dried to a consistency level of between 40% and 60%. Drying the fibers to within these preferred ranges generally will facilitate defibration of the fibers into individualized form without excessive formation of knots associated with higher moisture levels and without high levels of fiber damage associated with lower moisture levels.

For exemplary purposes, dewatering may be accomplished by such methods as mechanically pressing, centrifuging, or air drying the pulp. Additional drying is preferably performed by such methods, known in the art as air drying or flash drying, under conditions such that the utilization of high temperature for an extended period of time is not required. Excessively high temperature at this state of the process may result in the premature initiation of crosslinking. Preferably, temperatures in excess of 160°C are not maintained for periods of time in excess of 2 to 3 seconds. Mechanical defibration is performed as previously described.

The defibrated fibers are then heated to a suitable temperature for an effective period of time to cause the crosslinking agent to cure, i.e., to react with the cellulosic fibers. The rate and degree of crosslinking depends upon dryness of the fibers, temperature, amount and type of catalyst and crosslinking agent and the method utilized for heating and/or drying the fibers while crosslinking is performed. Crosslinking at a particular temperature will occur at a higher rate for fibers of a certain initial moisture content when accompanied by a continuous air through drying than when subjected to drying/heating in a static oven. Those skilled in the art will recognize that a number of temperature-time relationships exist for the curing of the crosslinking agent. Conventional paper drying temperatures, (e.g., 120°C to about 150°C), for periods of between 30 minutes and 60 minutes, under static, atmospheric conditions will generally provide acceptable curling efficiencies for fibers having moisture contents less than 5%. Those skilled in the art will also appreciate that higher temperatures and air convection decrease the time required for curing. However, curing temperatures are preferably maintained at less than 160°C, since exposure of the fibers to such high temperatures in excess of 160°C may lead to yellowing or other damaging of the fibers.

The maximum level of crosslinking will be achieved when the fibers are essentially dry (having less than 5% moisture). Due to this absence of water, the fibers are crosslinked while in a substantially unswollen, collapsed state. Consequently, they characteristically have low fluid retention values (FRV) relative to the range applicable to this invention. The FRV refers to the amount of fluid calculated on a dry fiber basis, that remains absorbed by a sample of fibers that have been soaked and then centrifuged to remove interfiber fluid. (The FRV is further defined and the Procedure For Determining FRV, is described below.) The amount of fluid that the crosslinked fibers can absorb is dependent upon their ability to swell upon saturation or, in other words, upon their interior diameter or volume upon swelling to a maxi-

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num level. This, in turn, is dependent upon the level of crosslinking. As the level of intrafiber crosslinking increases for a given fiber and process, the FRV of the fiber will decrease until the fiber does not swell at all upon wetting. Thus, the FRV value of a fiber is structurally descriptive of the physical condition of the fiber at saturation. Unless otherwise expressly indicated, FRV data described herein shall be reported in terms of the water retention value (WRV) of the fibers. Other fluids, such as salt water and synthetic urine, may also be advantageously utilized as fluid medium for analysis. Generally, the FRV of a particular fiber crosslinked by procedures wherein curing is largely dependent upon drying, such as the present process, will be primarily dependent upon the crosslinking agent and the level of crosslinking. The WRV's of fibers crosslinked by this dry crosslinking process at crosslinking agent levels applicable to this invention are generally less than 50, greater than 25, and are preferably between 28 and 45. Bleached SSK fibers having between 0.5 mole % and 2.5 mole % glutaraldehyde reacted thereon, calculated on a cellulose anhydroglucose molar basis, have been observed to have WRV's respectively ranging from 40 to 28. The degree of bleaching and the practice of post-crosslinking bleaching steps have been found to affect WRV. This effect will be explored in more detail below. Southern softwood Kraft (SSK) fibers prepared by dry crosslinking processes known prior to the present invention, have levels of crosslinking higher than described herein, and have WRV's less than 25. Such fibers, as previously discussed, have been observed to be exceedingly stiff and to exhibit lower absorbent capabilities than the fibers of the present invention.

In another process for making individualized, crosslinked fibers by a dry crosslinking process, cellulosic fibers are contacted with a solution containing a crosslinking agent as described above. Either before or after being contacted with the crosslinking agent, the fibers are provided in a sheet form. Preferably, the solution containing the crosslinking agent also contains one of the catalysts applicable to dry crosslinking processes, also described above. The fibers, while in sheeted form, are dried and caused to crosslink preferably by heating the fibers to a temperature of between about 120°C and 160°C. Subsequent to crosslinking, the fibers are mechanically separated into substantially individual form. This is preferably performed by treatment with a fiber fluffing apparatus such as the one described in U.S. Patent No. 3,987,968 or may be performed with other methods for defibrating fibers as may be known in the art. The individualized, crosslinked fibers made according to this sheet crosslinking process are treated with a sufficient amount of crosslinking agent such

that between 0.5 mole % and 3.5 mole % crosslinking agent, calculated on a cellulose anhydroglucose molar basis and measured subsequent to defibration are reacted with the fibers in the form of intrafiber crosslink bonds. Another effect of drying and crosslinking the fibers while in sheet form is that fiber to fiber bonding restrains the fibers from twisting and curling with increased drying. Compared to individualized, crosslinked fibers made according to a process wherein the fibers are dried under substantially unrestrained conditions and subsequently crosslinked in a twisted, curled configuration, absorbent structures made the relatively untwisted fibers made the sheet curing process described above would be expected to exhibit lower wet resiliency and lower responsiveness to wetting of a dry absorbent structure.

Another category of crosslinking processes applicable to the present invention is nonaqueous solution cure crosslinking processes. The same types of fibers applicable to dry crosslinking processes may be used in the production of nonaqueous solution crosslinked fibers. The fibers are treated with a sufficient amount of crosslinking agent such that between 0.5 mole % and 3.5 mole % crosslinking agent subsequently react with the fibers, wherein the level of crosslinking agent reacted is calculated subsequent to said crosslinking reaction, and with an appropriate catalyst. The crosslinking agent is caused to react while the fibers are submerged in a solution which does not induce any substantial levels of swelling of the fibers. The fibers, however, may contain up to 30% water, or be otherwise swollen in the crosslinking solution to a degree equivalent to fibers having a 30% moisture content. Such partially swollen fiber geometry has been found to provide additional unexpected benefits as hereinafter more fully discussed. The crosslinking solution contains a nonaqueous, water-miscible, polar diluent such as, but not limited to, acetic acid, propanoic acid, or acetone. Preferred catalysts include mineral acids, such as sulfuric acid, and halogen acids, such as hydrochloric acid. Other applicable catalysts include salts of mineral acids and halogen acids, organic acids and salts thereof. Crosslinking solution systems applicable for use as a crosslinking medium also include those disclosed in U.S. Patent No. 4,035,147, Issued to S. Sengenis, G. Guiray, and J. Quere, on July 12, 1977.

The crosslinking solution may include some water or other fiber swelling liquid, however, the amount of water is preferably insufficient to cause a level of swelling corresponding to that incurred by 70% consistency pulp fibers (30% aqueous moisture content). Additionally, crosslinking solution water contents less than 10% of the total volume of

the solution, exclusive of fibers are preferred. Levels of water in the crosslinking solution in excess of this amount decrease the efficiency and rate of crosslinking.

Absorption of crosslinking agent by the fibers may be accomplished in the crosslinking solution itself or in a prior treatment state including, but not limited to, saturation of the fibers with either an aqueous or nonaqueous solution containing the crosslinking agent. Preferably, the fibers are mechanically defibrated into individual form. This mechanical treatment may be performed by methods previously described for fluffing fibers in connection with the previously described dry crosslinking process.

It is especially preferred to include in the production of fluff a mechanical treatment which causes the moist cellulosic fibers to assume a curled or twisted condition to a degree in excess of the amount of curl or twist, if any, of the natural state of the fibers. This can be accomplished by initially providing fibers for fluffing which are in a moist state, subjecting the fibers to a mechanical treatment such as those previously described methods for defibrating the fibers into substantially individual form, and at least partially drying the fibers.

The relative amounts of curl and twist imparted to the fibers is in part dependent upon the moisture content of the fibers. Without limiting the scope of the invention, it is believed that the fibers naturally twist upon drying under conditions wherein fiber to fiber contact is low, i.e., when the fibers are in an individualized form. Also mechanical treatment of moist fibers initially causes the fibers to become curled. When the fibers are then dried or partially dried under substantially unrestrained conditions, they become twisted with the degree of twist being enhanced by the additional amount of curl mechanically imparted. The defibration fluffing steps are preferably practiced on high consistency moist pulp or pulp which has been dewatered to fiber consistency of 45% to 55% (determined prior to initialization of defibration).

Subsequent to defibration, the fibers should be dried to between 0% and 30% moisture content prior to being contacted with the crosslinking solution, if the defibration step has not already provided fibers having moisture contents within that range. The drying step should be performed while the fibers are under substantially unrestrained conditions. That is, fiber to fiber contact should be minimized so that the twisting of the fibers inherent during drying is not inhibited. Both air drying and flash drying methods are suitable for this purpose.

The individual fibers are next contacted with a crosslinking solution which contains a water-miscible, nonaqueous diluent, a crosslinking agent and a catalyst. The crosslinking solution may contain a limited amount of water. The water content of the crosslinking solution should be less than 18% and is preferably less than 9%.

A bat of fibers which have not been mechanically defibrated may also be contacted with a crosslinking solution as described above.

The amounts of crosslinking agent and acid catalyst utilized will depend upon such reaction conditions as consistency, temperature, water content in the crosslinking solution and fibers, type of crosslinking agent and diluent in the crosslinking solution, and the amount of crosslinking desired. Preferably, the amount of crosslinking agent utilized ranges from .2 wt % to 10 wt % (based upon the total, fiber-free weight of the crosslinking solution). Preferred acid catalyst content is additionally dependent upon the acidity of the catalyst in the crosslinking solution. Good results may generally be obtained for catalyst content, including hydrochloric acid, between .3 wt % and 5 wt % (fiber-free crosslinking solution weight basis) in crosslinking solutions containing an acetic acid diluent, preferred levels of glutaraldehyde, and a limited amount of water. Slurries of fibers and crosslinking solution having fiber consistencies of less than 10 wt % are preferred for crosslinking in conjunction with the crosslinking solutions described above.

The crosslinking reaction may be carried out at ambient temperatures or, for accelerated reaction rates, at elevated temperatures preferably less than 40°C.

There are a variety of methods by which the fibers may be contacted with, and crosslinked in, the crosslinking solution. In one embodiment, the fibers are contacted with the solution which initially contains both the crosslinking agent and the acid catalyst. The fibers are allowed to soak in the crosslinking solution, during which time crosslinking occurs. In another embodiment, the fibers are contacted with the diluent and allowed to soak prior to addition of the acid catalyst. The acid catalyst subsequently is added, at which time crosslinking begins. Other methods in addition to those described will be apparent to those skilled in the art, and are intended to be within the scope of this invention.

Preferably, the crosslinking agent and the conditions at which crosslinking is performed are chosen to facilitate intrafiber crosslinking. Thus, it is advantageous for the crosslinking reaction to occur in substantial part after the crosslinking agent has had sufficient time to penetrate into the fibers. Reaction conditions are preferably chosen so as to avoid instantaneous crosslinking unless the cross-

crosslinking agent has already penetrated into the fibers. Periods of reaction during which time crosslinking is substantially completed over a period of about 30 minutes are preferred. Longer reaction periods are believed to provide minimal marginal benefit in fiber performance. However, both shorter periods, including substantially instantaneous crosslinking, and longer periods are meant to be within the scope of this invention.

It is also contemplated to only partially cure while in solution, and subsequently complete the crosslinking reaction later in the process by drying or heating treatments.

Following the crosslinking step, the fibers are drained and washed. Preferably, a sufficient amount of a basic substance such as caustic is added in the washing step to neutralize any acid remaining in the pulp. After washing, the fibers are defluidized and dried to completion. Preferably, the fibers are subjected to a second mechanical defibration step which causes the crosslinked fibers to curl, e.g., fluffing by defibration, between the defluidizing and drying steps. Upon drying, the curled condition of the fibers imparts additional twist as previously described in connection with the curling treatment prior to contact with the crosslinking solution. The same apparatuses and methods for inducing twist and curl described in connection with the first mechanical defibration step are applicable to this second mechanical defibration step. As used herein, the term "defibration" shall refer to any of the procedures which may be used to mechanically separate the fibers into substantially individual form, even though the fibers may already be provided in such form. "Defibration" therefore refers to the step of mechanically treating the fibers, in either individual form or in a more compacted form, to a mechanical treatment step which a) would separate the fibers into substantially individual form if they were not already in such form, and b) imparts curl and twist to the fibers upon drying.

This second defibration treatment, after the fibers have been crosslinked, has been found to increase the twisted, curled character of the pulp. This increase in the twisted, curled configuration of the fibers leads to enhanced absorbent structure resiliency and responsiveness to wetting. A second defibration treatment may be practiced upon any of the crosslinked fibers described herein which are in a moist condition. However, it is a particular advantage of the nonaqueous solution crosslinking method that a second defibration step is possible without necessitating an additional drying step. This is due to the fact that the solution in which the fibers are crosslinked keep the fibers flexible subsequent to crosslinking even though not causing the fibers to assume an undesirable, highly swollen state.

It has been further unexpectedly found that increased degrees of absorbent structure expansion upon wetting compressed pads can be obtained for structures made from fibers which have been crosslinked while in a condition which is twisted but partially swollen relative to fibers which have been thoroughly dried of water prior to crosslinking.

Improved results are obtained for individualized, crosslinked fibers which have been crosslinked under conditions wherein the fibers are dried to between 18% and 30% water content prior to contact with the crosslinking solution. In the case wherein a fiber is dried to completion prior to being contacted with the crosslinking solution, it is in a nonswollen, collapsed state. The fiber does not become swollen upon contact with the crosslinking solution due to the low water content of the solution. As discussed before, a critical aspect of the crosslinking solution is that it does not cause any substantial swelling of the fibers. However, when the diluent of the crosslinking solution is absorbed by an already swollen fiber, the fiber is in effect "dried" of water, but the fiber retains its preexisting partially swollen condition.

For describing the degree to which the fiber is swollen, it is useful to again refer to the fluid retention value (FRV) of the fiber subsequent to crosslinking. Fibers having higher FRV's correspond to fibers which have been crosslinked while in a more swollen state relative to fibers crosslinked while in a less swollen state, all other factors being equal. Without limiting the scope of the invention, it is believed that partially swollen, crosslinked fibers with increased FRV's have greater wet resilience and responsiveness to wetting than fibers which have been crosslinked while in an unswollen state. Fibers having this increase in wet resilience and responsiveness to wetting are more readily able to expand or untwist when wetted in an attempt to return to their natural state. Yet, due to the stiffness imparted by crosslinking, the fibers are still able to provide the structural support to a saturated pad made from the fibers. Numerical FRV data described herein in connection with partially swollen crosslinked fibers shall be water retention values (WRV). As the WRV increases beyond approximately 60, the stiffness of the fibers is believed to become insufficient to provide the wet resilience and responsiveness to wetting desired to support a saturated absorbent structure.

In an alternative method of crosslinking the fibers in solution, the fibers are first soaked in an aqueous or other fiber swelling solution, defluidized, dried to a desired level and subsequently submerged in a water-miscible crosslinking solution containing a catalyst and crosslinking agent as previously described. The fibers are preferably me-

chanically defibrated into form subsequent to defluidization and prior to additional drying, in order to obtain the benefits of enhanced twist and curl as previously described. Mechanical defibration practiced subsequent to contacting the fibers with the crosslinking agent is less desirable, since such defibration would volatilize the crosslinking agent thus, possibly leading to atmospheric contamination by, or high air treatment investments due to, the crosslinking agent.

In a modification of the process described immediately above, the fibers are defibrated and then presoaked in a high concentration solution of crosslinking agent and a fiber-swelling diluent, preferably water. The crosslinking agent concentration is sufficiently high to inhibit water-induced swelling of fibers. Fifty percent, by weight, aqueous solutions of the crosslinking agents of this invention, preferably, glutaraldehyde, have been found to be useful solutions for presoaking the fibers. The presoaked fibers are defluidized and submerged in a crosslinking solution containing a water-miscible, polar diluent, a catalyst, and a limited amount of water, and then crosslinked as previously described. Also as described above, the crosslinked fibers may be defluidized and subjected to a second mechanical defibration step prior to further processing into a sheet or absorbent structure.

Presoaking the fibers with crosslinking agent in an aqueous solution prior to causing the crosslinking agent to react provides unexpectedly high absorbency properties for absorbent pads made from the crosslinked fibers, even relative to pads made from crosslinked fibers of the prior described nonaqueous solution cure processes wherein the fibers were not presoaked with a solution containing crosslinking agent.

The crosslinked fibers formed as a result of the preceding dry crosslinking and nonaqueous solution crosslinking processes are the product of the present invention. The crosslinked fibers of the present invention may be utilized directly in the manufacture of air laid absorbent cores. Additionally, due to their stiffened and resilient character, the crosslinked fibers may be wet laid into an uncompacted, low density sheet which, when subsequently dried, is directly useful without further mechanical processing as an absorbent core. The crosslinked fibers may also be wet laid as compacted pulp sheets for sale or transport to distant locations.

Once the individualized, crosslinked fibers are made, they may be dry laid and directly formed into absorbent structures, or wet laid and formed into absorbent structures or densified pulp sheets. However, it is difficult to form such fibers into a smooth, wet laid sheet by conventional wet sheet formation practices. This is because individualized,

crosslinked fibers may flocculate when in solution. Such flocculation may occur both in the headbox and upon deposition into the foraminous forming wire. Attempts to sheet individualized, crosslinked fibers by conventional pulp sheeting methods have been found to result in the formation of a plurality of clumps of flocculated fibers. Without limiting the invention, it is believed that this results from the stiff, twisted character of the fibers, a low level of fiber to fiber bonding, and the high drainability of the fibers once deposited on a sheet forming wire. It is therefore a significant commercial concern that a practical process for sheeting individualized, crosslinked fibers be provided, whereby wet laid absorbent structures and densified pulp sheets for transit and subsequent defibration may be formed.

Accordingly, a novel process for sheeting individualized, crosslinked fibers which tend to flocculate in solution has been developed, wherein a slurry containing individualized, crosslinked fibers are initially deposited on a foraminous forming wire, such as a Fourdrinier wire in a manner similar to conventional pulp sheeting processes. However, due to the nature of individualized, crosslinked fibers, these fibers are deposited on the forming wire in a plurality of clumps of fibers. At least one stream of fluid, preferably water, is directed at the deposited, clumped fibers. Preferably, a series of showers are directed at the fibers deposited on the forming wire, wherein successive showers have decreasing volumetric flow rates. The showers should be of sufficient velocity such that the impact of the fluid against the fibers acts to inhibit the formation of flocculations of the fibers and to disperse flocculations of fibers which have already formed. The fiber setting step is preferably performed with a cylindrical screen, such as a dandy roll, or with another apparatus analogous in function which is or may become known in the art. Once set, the fibrous sheet may then be dried and optionally compacted as desired. The spacing of the showers will vary depending upon the particular rate of fiber floccing, line speed of the forming wire, drainage through the forming wire, number of showers, and velocity and flow rate through the showers. Preferably, the showers are close enough together so that substantial levels of floccing are not incurred.

In addition to inhibiting the formation of and dispersing flocculations of fibers, the fluid showered onto the fibers also compensates for the extremely fast drainage of individualized, crosslinked fibers, by providing additional liquid medium in which the fibers may be dispersed for subsequent sheet formation. The plurality of showers of decreasing volumetric flow rates facilitates a systematic net increase in slurry consistency while provid-

ing a repetitive dispersive and inhibiting effect upon flocculations of the fibers. This results in the formation of a relatively smooth and even deposition of fibers which are then promptly, i.e., before reflocculation, set into sheeted form by allowing the fluid to drain and pressing the fibers against the foraminous wire.

Relative to pulp sheets made from conventional, uncrosslinked cellulosic fibers, the pulp sheets made from individualized, crosslinked fibers are more difficult to compress to conventional pulp sheet densities. Therefore, it may be desirable to combine crosslinked fibers with uncrosslinked fibers, such as those conventionally used in the manufacture of absorbent cores. Pulp sheets containing stiffened, crosslinked fibers preferably contain between 5% and 90% uncrosslinked, cellulosic fibers, based upon the total dry weight of the sheet, mixed with the individualized, crosslinked fibers. It is especially preferred to include between 5% and 30% of highly refined, uncrosslinked cellulosic fibers, based upon the total dry weight of the sheet. Such highly refined fibers are refined or beaten to a freeness level less than 300 ml CSF, and more preferably less than 100 ml CSF. The uncrosslinked fibers are preferably mixed with an aqueous slurry of the individualized, crosslinked fibers. This mixture may then be formed into a densified pulp sheet for subsequent defibration and formation into a absorbent pads. The incorporation of the uncrosslinked fibers eases compression of the pulp sheet into a densified form, while imparting a surprisingly small loss in absorbency to the subsequently formed absorbent pads. The uncrosslinked fibers additionally increase the tensile strength of the pulp sheet and to absorbent pads made either from the pulp sheet or directly from the mixture of crosslinked and uncrosslinked fibers. The blend of crosslinked and uncrosslinked fibers may be first made into a pulp sheet and then comminuted to form an absorbent pad or formed directly utilized as an absorbent pad. The fibers, if comminuted, may be air-laid or wet-laid as previously described.

Wet-laid sheets or webs made from the individualized, crosslinked fibers, or from mixtures also containing uncrosslinked fibers, will preferably have basis weights of less than 800 g/m² and densities of less than 0.60 g/cm³. Although it is not intended to limit the scope of the invention, sheets having basis weights between 300g/m² and 600 g/m² and densities between 0.15 g/cc and 0.3 g/cc are especially contemplated for direct application as absorbent cores in disposable articles such as diapers, tampons, and other catamenial products. Structures having basis weights and densities higher than these levels are believed to be most useful for subsequent comminution and air-laying or wet-laying to form a lower density and basis weight struc-

ture which is more ideal for absorbent applications. Other applications contemplated for the fibers of the present invention include low density tissue sheets having densities which may be less than 0.10 g/cc.

The absorbent structures made by the process described are useful for a variety of absorbent articles including, but not limited to, tissue sheets, disposable diapers, catamenials, sanitary napkins, tampons, and bandages wherein each of said articles has an absorbent structure containing the individualized, crosslinked fibers described herein. For example, a disposable diaper or similar article having a liquid permeable topsheet, a liquid impermeable backsheet connected to the topsheet, and an absorbent structure containing individualized, crosslinked fibers is particularly contemplated. Such articles are described generally in U.S. Patent 3,860,003, Issued to Kenneth B. Buell on January 14, 1975.

PROCEDURE FOR DETERMINING FLUID RETENTION VALUE

The following procedure was utilized to determine the water retention value of cellulosic fibers.

A sample of 0.3 g to 0.4 g of fibers is soaked in a covered container with 100 ml distilled or deionized water at room temperature for between 15 and 20 hours. The soaked fibers are collected on a filter and transferred to an 80-mesh (opening 0.177mm) wire basket supported 38mm. above a 60-mesh (opening 0.25mm) screened bottom of a centrifuge tube. The tube is covered with a plastic cover and the sample is centrifuged at a relative centrifuge force of 1500 to 1700 gravities for 19 to 21 minutes. The centrifuged fibers are then removed from the basket and weighed. The weighed fibers are dried to a constant weight at 105°C and reweighed. The water retention value is calculated as follows:

$$(1) \text{ WRV} = \frac{(W-D)}{D} \times 100$$

where,

W = wet weight of the centrifuged fibers;

D = dry weight of the fibers; and

W-D = weight of absorbed water.

PROCEDURE FOR DETERMINING LEVEL OF GLUTARALDEHYDE REACTED WITH CELLULOSIC FIBERS

The following procedure was utilized to determine the level of glutaraldehyde which reacted to form Intrafiber crosslink bonds with the cellulosic component of the Individualized, glutaraldehyde-crosslinked fibers.

A sample of individualized, crosslinked fibers is extracted with 0.1N HCl at 60°C for one hour. The extract is separated from the fibers, and the same extraction/separation procedure is then repeated for each sample an additional three times. The extract from each extraction is separately mixed with an aqueous solution of 2,4-dinitrophenylhydrazone (DNPH). The reaction is allowed to proceed for 15 minutes after which a volume of chloroform is added to the mixture. The reaction mixture is mixed for an additional 45 minutes. The chloroform and aqueous layers are separated with a separatory funnel. The level of glutaraldehyde is determined by analyzing the chloroform layer by high pressure liquid chromatography (HPLC) for DNPH derivative.

The chromatographic conditions for HPLC analysis utilized were - Column: C-18 reversed phase; Detector: UV at 360 nm; Mobile phase 80:20 methanol; Flow rate: 1 ml/min.; measurement made: peak height. A calibration curve of peak height and glutaraldehyde content was developed by measuring the HPLC peak heights of five standard solutions having known levels of glutaraldehyde between 0 and 25 ppm.

Each of the four chloroform phases for each fiber sample was analyzed by HPLC, the peak height measured, and the corresponding level of glutaraldehyde determined from the calibration curve. The glutaraldehyde concentrations for each extraction were then summed and divided by the fiber sample weight (dry fiber basis) to provide glutaraldehyde content on a fibers weight basis.

Two glutaraldehyde peaks were present for each of the HPLC chromatograms. Either peak may be used, so long as that same peak is used throughout the procedure.

EXAMPLE 1

This example discloses a preferred process for making Individualized, crosslinked fibers. The individualized, crosslinked fibers were made by a dry crosslinking process.

For each sample, a quantity of never dried, southern softwood kraft (SSK) pulp were provided. The fibers had a moisture content of 62.4% (equivalent to 37.6% consistency). A slurry was

formed by adding the fibers to a solution containing a selected amount of 50% aqueous solution of glutaraldehyde, 30% (based upon the weight of the glutaraldehyde) zinc nitrate hexahydrate, demineralized water and a sufficient amount of 1N HCl to decrease the slurry pH to 3.7. The fibers were soaked in the slurry for a period of 20 minutes and then dewatered to a fiber consistency of 34% to 35% by centrifuging. Next, the dewatered fibers were air dried to a fiber consistency of 55% to 56% with a blow through dryer utilizing ambient temperature air. The air dried fibers were defibrated utilizing a three-stage fluffing device as described in U.S. Patent 3,987,968. The defibrated fibers were placed in trays and cured at 145°C in an essentially static drying oven for a period of 45 minutes. Crosslinking was completed during the period in the oven. The crosslinked, individualized fibers were placed on a mesh screen and washed with 20°C water, soaked at 1% consistency for one (1) hour in 60°C water, screened, washed with 20°C water for a second time, centrifuged to 60% fiber consistency, defibrated in a three stage fluffer as previously described, and dried to completion in a static drying oven at 105°C for four (4) hours. The fibers had between 0 mole % and 3.3 mole % glutaraldehyde reacted in the form of crosslink bonds. The corresponding WRV's varied between 51% and 28%.

Example

The purpose of this example is to exemplify a process for making wet-laid sheets containing individualized, crosslinked fibers.

A 0.55% consistency slurry of a blend of fibers containing 90% individualized, crosslinked fibers made according to the crosslinking process described in Example 1 and 10% conventional, uncrosslinked fibers having a freeness of less than 100 CSF were deposited in flocculated, clumped fibers on a conventional 84-mesh Fourdiner forming wire. The papermaking flow rate out of the headbox was 430 kg/min. Immediately after deposition, a series of five streams of water of sequentially decreasing flow rates were directed upon the fibers. The five streams of water provided a cumulative flow ratio 85 kg water/kg bone dry (b.d.) fiber. The showers were all spaced within an approximately 1 meter long area parallel to the direction of travel of the forming wire. Each stream of water was showered onto the fibers through a linear series of 1/8" (3.2 mm) ID circular apertures spaced 1/2" (12.7 mm) apart and extending across the width of the forming wire. The approximate percentage of flow, based upon the total flow rate, and velocity of flow through the apertures for each of

the showers was as follows: Shower 1-37% of total flow, 170 m/min.; Shower 2-20% of total flow, 165 m/min.; Shower 3-13% of total flow, 61 m/min.; Shower 4-9% of total flow, 41 m/min.; Shower 5-5% of total flow, 20 m/min. Immediately after the fifth shower, the fibers were set by treatment with a cylindrical, screened roll known in the art as a Dandy Roll. The Dandy Roll pressed the fibers, which at the time of setting were in a high consistency slurry form, against the forming wire to set the fibers to form a wet sheet. The sheet was similar in appearance to conventional fibrous pulp sheets.

Claims

1. A process for making a sheet containing individualized, stiffened fibers which characteristically flocculate in solution, said process comprising the steps of:

a) providing a fibrous slurry containing individualized, stiffened fibers and a fluid medium;

b) depositing said slurry on a foraminous forming wire;

c) directing at least one stream of fluid upon said fibers deposited on said forming wire and draining the fluid from said fibers, wherein said stream of fluid disperses flocculations of said fibers and inhibits formation of flocculations of said fibers, to provide said fibers in substantially unflocculated form; and

d) setting said fibers in sheeted form, subsequent to step c), while said fibers are in substantially unflocculated form.

2. A process according to Claim 1, wherein the step of setting said fibers in sheeted form is performed by pressing said fibers against said forming wire with a screened, cylindrical roll.

3. A process according to either one of Claims 1 & 2, wherein a plurality of streams of fluid having sequentially decreasing volumetric flow rates are directed upon said fibers.

4. A process according to any one of Claims 1-3, wherein said fibers are crosslinked fibers.

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PROCEDURE FOR DETERMINING LEVEL OF GLUTARALDEHYDE REACTED WITH CELLULOSIC FIBERS

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